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A NEW CARBON DIOXIDE SENSING METHOD SUITABLE FOR USE  
IN MICROELECTRODE SENSORS

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method is not conducive to miniaturization and it is susceptible to the same basic problems associated with the pH-electrode, i.e. low sensitivity, slow response and considerable drift.

The feasibility of developing a new electrochemical carbon dioxide sensing method based on the reductive adsorption of  $\text{CO}_2$  onto a noble metal electrode and the subsequent anodic oxidation of the "Reduced- $\text{CO}_2$ " species has been investigated experimentally. In this approach, the total charge required to oxidize the chemisorbed "Reduced- $\text{CO}_2$ " species is measured. This amount is proportional to the  $\text{CO}_2$  concentration in the immediate neighborhood of the electrode surface and can also be made a function of  $\text{CO}_2$  partial pressure in the environment.

The physical sensor configuration chosen for this feasibility study is a modification of that of a Clark oxygen sensor. The electrodes are separated from the environment by a gas permeable (electrolyte impermeable) hydrophobic membrane. Behind this membrane, on the electrode side, an internal electrolyte which can equilibrate with  $\text{CO}_2$  is used. In addition to the working (sensing) and counter electrodes, a reference electrode (either located internally or connected externally through an electrolyte bridge) must be used.

We have fabricated two prototype sensors of different configurations. Their  $\text{CO}_2$  sensing capabilities were determined in liquids containing dissolved  $\text{CO}_2$  as well as in gases. The effects of electrode roughness factor, internal electrolyte composition, membrane permeability, and sensor configuration have been carefully investigated. The optimal electrical parameters defining the potential-time relationships of the potential pulses used in the measurements have been determined for the  $P_{\text{CO}_2}$  range from 7.6 to 760 mm Hg.

These parameters, of course, can be further optimized for a specific range of interest for better sensitivity and/or faster response time.

The "Reduced- $\text{CO}_2$ " oxidation charge was indeed found to be a sensitive and reproducible function of  $P_{\text{CO}_2}$  in all cases. This new electrochemical sensing method worked equally effectively in measuring  $\text{CO}_2$  in liquids as well as in gases.

Furthermore, the same sensor was found to be capable of concurrently but independently determining the oxygen partial pressure in a fluid. This was accomplished by measuring the limiting current of oxygen reduction immediately following the measurement of "Reduced- $\text{CO}_2$ " oxidation charge. Perhaps more importantly, it was established that under proper conditions the presence of oxygen does not interfere with the measurement of  $\text{CO}_2$  concentration.

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## I. INTRODUCTION

Presently employed electrochemical  $\text{CO}_2$ -sensors, whether they are intended for implantation, IN-VITRO, or transcutaneous applications, are basically modified pH-electrodes; the operating principle of which is based on the measurement of a potential that is effectively a linear function of the logarithm of  $\text{H}^+$  ion concentration as demonstrated by Stow and Randall (1), and Gertz and Loeschke (2). In Severinghaus' approach (3), the sensor consists of a flat-surfaced glass pH-electrode covered with a hydrophobic membrane such as Teflon, which is permeable to  $\text{CO}_2$ , but not to  $\text{H}^+$ . Between the glass electrode surface and Teflon membrane there is a paper spacer holding the electrolyte, typically 10mM  $\text{NaHCO}_3$  in 0.1M  $\text{NaCl}$ . The relationship between pH and  $P_{\text{CO}_2}$  in this sensor is  $\Delta \text{pH} = 0.97 \Delta \log_{10} P_{\text{CO}_2}$ . The factor of 0.97 takes into consideration buffering, mostly by  $\text{CO}_3^{=}$ . Since one unit of pH at room temperature corresponds to less than 60mV potential change, it is obvious that the  $P_{\text{CO}_2}$  measurement is intrinsically inaccurate (a change of  $P_{\text{CO}_2}$  by a factor of 2 corresponds to 18mV change). In addition, the method is not conducive to miniaturization. A possibility for  $\text{CO}_2$ -sensor miniaturization, based on a pH measurement, would be to substitute the glass electrode with miniature  $\text{H}^+$  electrodes with Pd/PdO wire or an electrode with an ion selective liquid membrane (4). Another possibility would be the use of solid state CHEMFET  $\text{H}^+$  electrodes (5).

Both cases, however, show the same basic problems of the glass electrode i.e. low sensitivity, together with very slow

response and considerable drift.

Because of the problems of the potentiometric method, with its small voltage changes for sizeable change in  $P_{CO_2}$ , it appears that a current or charge method in which the signal is a function of  $P_{CO_2}$  would be advantageous. In this program we have investigated the feasibility of a novel carbon dioxide sensing method based on the reductive adsorption of  $CO_2$  on platinum (or other noble metal) electrode to form the "Reduced- $CO_2$ " species discovered by J. Giner in 1962 (6).



where  $Pt\text{-"Reduced-}CO_2\text{"}$  represents the chemisorbed "Reduced- $CO_2$ " species. This species was the object of considerable interest by a number of electrochemists in the late sixties in the context of direct hydrocarbon fuel cell research (7). The charge required to oxidize this species is proportional to the coverage of "Reduced- $CO_2$ " which can be made a function of carbon dioxide partial pressure in the environment.

The main objective of this work was the development of a novel electrochemical method to determine  $CO_2$  concentration based on the principle described above. Specifically, it involves measuring the amount of "Reduced- $CO_2$ " formed on a platinum electrode surface under conditions such that this amount is a function of  $P_{CO_2}$ .

The typical sensor configuration chosen for this work is similar to that of a Clark electrode (sensor) for oxygen



measurement, in which the electrodes are separated from the environment by a hydrophobic membrane which is impermeable to electrolyte, but permeable to gas. Behind this membrane, on the electrode side, there is an electrolyte which can be equilibrated with  $\text{CO}_2$  (e.g. acid, bicarbonate solution with an inert salt, etc.). For this application, in addition to the working electrode and the counter electrode, a reference electrode (either located internally or externally) is used.

The actual measurement is potentiodynamic involving the consecutive application of at least two (perhaps three) potential pulses, over a short period of time, to the working (sensing) electrode using a potentiostat:

a) The "Reduced- $\text{CO}_2$ " forming potential pulse of controlled magnitude and duration at which this chemisorbed species is formed.

The amount of "Reduced- $\text{CO}_2$ " is a function of the electrode potential, electrode roughness factor, duration, and  $\text{CO}_2$  concentration in the immediate neighborhood of the electrode. The latter is related to the  $P_{\text{CO}_2}$  of the external fluid and depends on the mass transport characteristics of the membrane. In a "membrane limited" sensor, the amount of "Reduced- $\text{CO}_2$ " formed per unit of time before saturation will depend on the membrane permeability. In addition,  $\text{CO}_2$  could be determined by using kinetic rates of "Reduced- $\text{CO}_2$ " formation or by using the isotherm between "Reduced- $\text{CO}_2$ " coverage and  $\text{CO}_2$  concentration.

b) The measuring potential pulse during which the charge due to the oxidation of "Reduced- $\text{CO}_2$ " is measured.

This charge is a function of  $P_{CO_2}$  and can be obtained by electronically integrating the current in the relevant potential region and converted to calibrated  $P_{CO_2}$  units. If necessary, an additional potential pulse will be added.

c) The activating (or cleaning) potential pulse during which the electrode surface is cleansed of any impurities by applying a high (anodic) potential.

Because of the presence of a hydrophobic membrane, there should be no inhibitor or co-reactant effect of non-volatile materials during the measurement. Oxygen interaction can be kept low because this method integrates current for "Reduced- $CO_2$ " oxidation, and the current due to oxygen reduction is not integrated. In addition, measurements of charge difference with and without adsorbed "Reduced- $CO_2$ " makes  $O_2$ -effect even smaller.

In addition, as a secondary but important objective, the substantially concurrent but independent determination of carbon dioxide and oxygen concentrations using the same sensor was investigated. (Oxygen concentration can be determined by measuring the limiting current due to oxygen reduction.) It is envisioned that the sensor in the proper configuration is suitable for  $CO_2$  (and  $O_2$ ) determination in gases and liquids, and also is conducive to miniaturization for implantation in tissue and blood vessels.

## II. EXPERIMENTAL

### A. Sensor Design and Fabrication

Two different sensor configurations were adopted in this program. Actual laboratory prototype CO<sub>2</sub> sensors were fabricated based on both designs. The first configuration (a two-electrode sensor) does not contain an internal reference electrode. This design, however, could still become a practical configuration to measure dissolved CO<sub>2</sub> content in liquids in conjunction with an external reference electrode. The second design (a three-electrode sensor) is a self-contained sensor configuration complete with a built-in electrolyte reservoir. This design allows the measurement of CO<sub>2</sub> content both in solutions and in gases over extended periods of time. The details of these two sensor configurations are given in the following:

#### 1. Two Electrode Sensors

Two-electrode sensors were fabricated by embedding the working and the counter electrodes in the base of a cylinder of resin (e.g. Quickmount, Fisher Scientific) as schematically shown in Figure 1. It consists of a rectangularly shaped platinum working electrode, approximately 1.25 mm x 6 mm, which is sandwiched by two interconnected platinum counter electrodes of similar shape and size. The resultant electrode surface was ground flush with SiC paper and then polished with 0.3 $\mu$  alumina on emery cloth to yield a smooth surface. Alternatively, the surface of the platinum electrodes could also be platinized to give surface roughness factor of about 120 to provide more advantageous response in sensing CO<sub>2</sub>.

Either a 250 $\mu$  thick micro-quartz glass fiber (Gelman Scientific, Inc.) or a 125 $\mu$  thick non-woven glass fiber (Mead Corp.) spacer pre-wetted with the internal electrolyte was placed over the electrode surface and a 25 $\mu$  thick Teflon membrane (Goretex, 0.2 pore size, W.L. Gore & Assoc., Inc.) was mounted over the wetted spacer to separate the internal electrolyte from the exterior environment. The reference electrode bridge was filled with glass fiber to minimize convection.

## 2. Three-Electrode Sensors

This "self-contained" CO<sub>2</sub> sensor is essentially a modified Clark oxygen sensor (which is a two-electrode system) as shown schematically in Figure 2. It consists of a platinized platinum disc working electrode (0.047 cm<sup>2</sup> geometric area, roughness factor  $\sim$  125) and a Teflon-bonded platinum ring used as the counter electrode which is placed immediately behind the working electrode. The reference electrode, in this case, is a dynamic hydrogen electrode which is contained in a Teflon tube to minimize the effect of hydrogen and oxygen bubbles evolved during its operations. This reference electrode is immersed in the internal electrolyte reservoir. This design enables the sensor to operate with or without a paper spacer over an extended period of time.

### B. Electrochemical Measurement of CO<sub>2</sub> Dissolved in a Liquid

All the experiments were carried out in a jacketed electrochemical cell at 37°C. Premixed and preanalyzed CO<sub>2</sub> containing gas mixtures which covered a wide P<sub>CO<sub>2</sub></sub> range from 7.6 to 760 mm Hg were used in this work. The gas first passed through a pre-saturator (also maintained at 37°C) before entering the cell and it was allowed to equilibrate for at least 20 minutes before any measurement was made for a new gas composition.

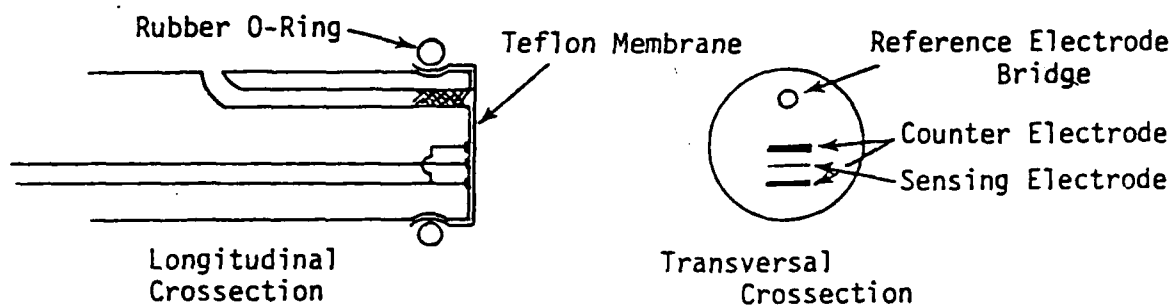


Figure 1. Schematic Diagram of a Two-Electrode Sensor.

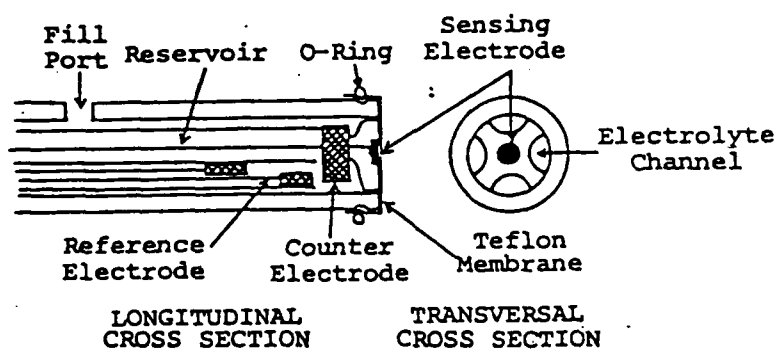


Figure 2. Schematic Diagram of a Three-Electrode Self-Contained Sensor.

The  $\text{CO}_2$  sensing capability in solutions containing dissolved  $\text{CO}_2$  has been determined in 1M  $\text{H}_2\text{SO}_4$  and Krebs-Ringer solution (see Table 1 for its composition). The internal electrolytes studied included (a) 1M  $\text{H}_2\text{SO}_4$ ; (b) 0.02M  $\text{KHCO}_3$  and 0.05M  $\text{Na}_2\text{SO}_4$  (c) 0.025M  $\text{Na}_2\text{HPO}_4$ , 0.025M  $\text{KH}_2\text{PO}_4$ , and 0.1M  $\text{NaClO}_4$  and (d) 0.05M  $\text{H}_2\text{SO}_4$  and 0.1M  $\text{Na}_2\text{SO}_4$ .

Figure 3 shows a schematic block diagram of the electrochemical measuring system. A PAR 173 potentiostat, a HP 3310B function generator, and a HP 7047A X-Y recorder were used in this work. If an external reference electrode was needed (for a two-electrode sensor), a dynamic hydrogen electrode (DHE) was used when the  $\text{CO}_2$  containing liquid was 1M  $\text{H}_2\text{SO}_4$ . When Krebs-Ringer was the external solution, a saturated calomel electrode (SCE) was used as the reference. The working electrode was first activated (cleaned) before each measurement by cycling from 0 to 1500 mV versus the reversible hydrogen electrode (RHE), using a triangular waveform at a sweep rate of 500 mV/sec. The potential of the working electrode was then held at  $E_{\text{ads}}$  for a period of time ( $t_{\text{ads}}$ ) to allow the reductive adsorption of  $\text{CO}_2$  to take place. It was then followed by an anodic potential ramp to oxidize the "Reduced- $\text{CO}_2$ " species formed on the electrode. The current-potential response curve was recorded so that the total charge passed due to the oxidation of "Reduced- $\text{CO}_2$ " could be integrated and plotted vs.  $P_{\text{CO}_2}$  to obtain a calibration curve. Both sensor configurations were used to determine dissolved  $\text{CO}_2$  contents in liquids.

#### C. Electrochemical Measurement of $\text{CO}_2$ in the Gas Phase

For measuring the partial pressure of carbon dioxide in the gas

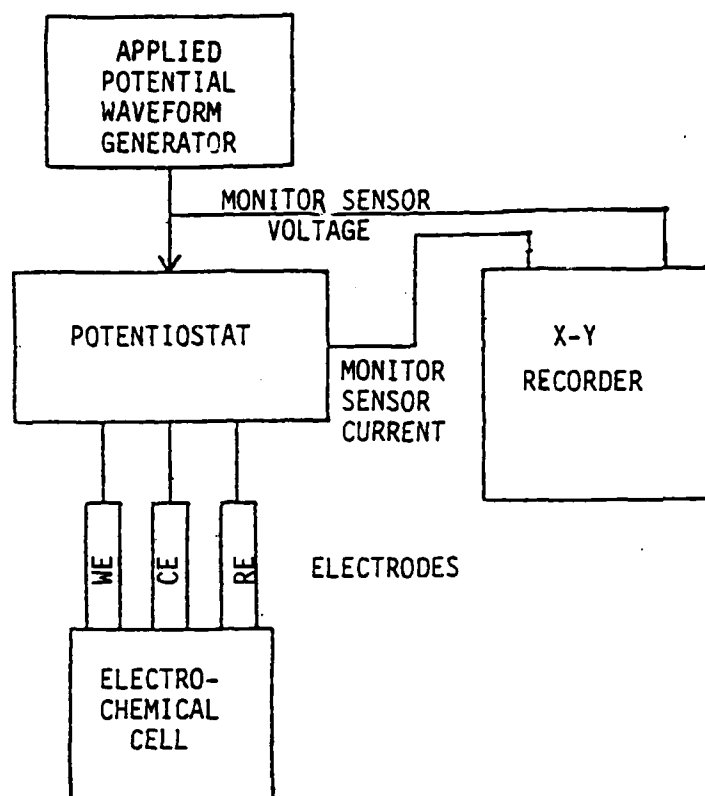


Figure 3. Block Diagram of Electrochemical Measuring System.

phase, only the three-electrode sensors could be used. The experimental set-up was exactly the same as that described in the earlier section. The only difference was that the gas mixture was allowed to pass through a pre-saturator partially filled with a solution of the same composition as the internal electrolyte of the sensor. It was then introduced to a small volume glass vessel from the bottom with the sensor inserted in the vessel from the top. All the gas phase measurements were carried out at ambient temperature.

TABLE 1  
COMPOSITION OF KREBS-RINGER SOLUTION

NaCl	0.109M
KCl	0.004M
NaHCO	0.024M
MgSO	0.0006M
NaH PO	0.001M



### III. RESULTS AND DISCUSSION

#### A. Electrochemical Sensing of CO<sub>2</sub> Dissolved in a Liquid Using Smooth Platinum Electrodes

Preliminary measurements were carried out using the two-electrode sensor with smooth platinum electrodes to determine the CO<sub>2</sub> content in a 1M H<sub>2</sub>SO<sub>4</sub> solution at 37°C. The internal electrolyte was also 1M H<sub>2</sub>SO<sub>4</sub>. We studied the effect of E<sub>ads</sub> (from 20 to 270 mV vs. RHE in 50 mV increments), t<sub>ads</sub> (from 10 to 300 sec.), and the anodic sweep rate (from 150 to 9600 mV/sec) on the current-potential response curve in the region of "Reduced-CO<sub>2</sub>" oxidation. The oxidation current peak was found to be in the 900-1100 mV (vs. RHE) region depending on E<sub>ads</sub> and the sweep rate. The position of the oxidation current peak shifted toward lower potentials as E<sub>ads</sub> become less positive and with decreasing sweep rate. Figure 4 shows the current-potential curve of this sensor in response to the presence of 760 mm Hg of CO<sub>2</sub> in the external solution as a function of t<sub>ads</sub>. As expected, the oxidation current peak increased with adsorption time up to a limit (e.g. 5 minutes in this case) beyond which no further change occurred because complete coverage of "Reduced-CO<sub>2</sub>" had been realized.

It was also demonstrated that under certain conditions the oxidation current did depend on P<sub>CO<sub>2</sub></sub>. For example, with E<sub>ads</sub> = 70 mV (vs. RHE), t<sub>ads</sub> = 120 sec and sweep rate = 3600 mV/sec, the oxidation current peak was found to be at 950 mV (vs. RHE) with a maximum current density of 21.3 mA/cm<sup>2</sup> under 100% CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub> = 760 mm Hg) as shown in Figure 5a. For 5% CO<sub>2</sub> 95% nitrogen, (P<sub>CO<sub>2</sub></sub> = 38 mm Hg), a much smaller oxidation current peak was observed with a

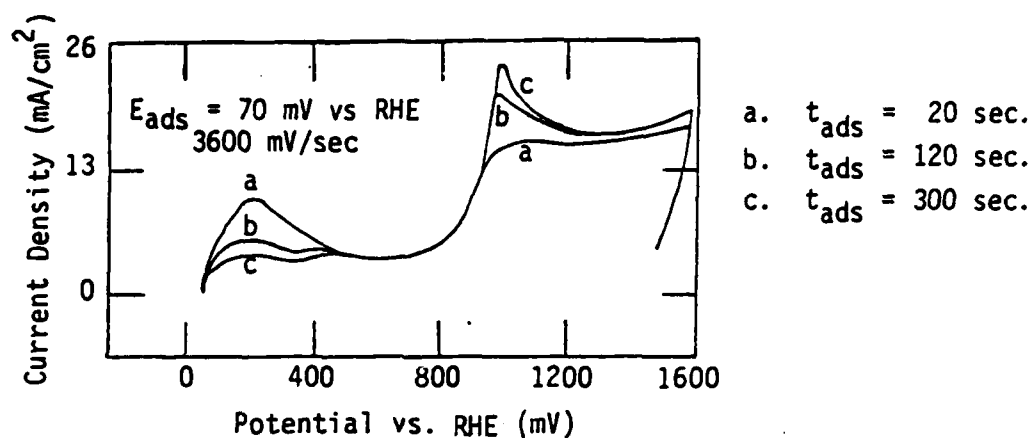


Figure 4. Current-Potential Curves of a Two-Electrode  $\text{CO}_2$  Sensor with Smooth Pt Electrodes at 760 mm Hg  $\text{CO}_2$ .

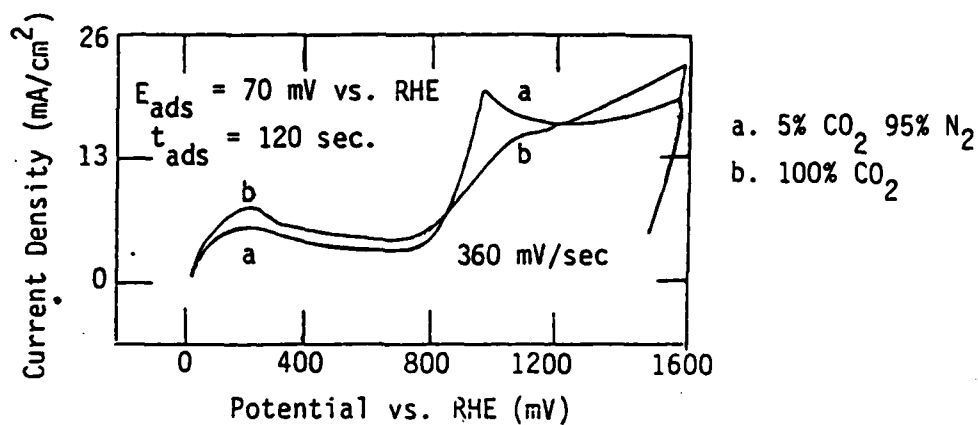


Figure 5. Current-Potential Curves of a Two-Electrode  $\text{CO}_2$  Sensor with Smooth Pt Electrodes at 38 and 760 mm Hg  $\text{CO}_2$ .

corresponding current density of  $14.7 \text{ mA/cm}^2$  at the same potential, (see Figure 5b).

These results have already demonstrated the validity of the concept of determining the partial pressure of  $\text{CO}_2$  by measuring the amount of "Reduced- $\text{CO}_2$ " adsorbed on a working electrode. In practice, however, it is more desirable to have the "Reduced- $\text{CO}_2$ " oxidation current peak located in the "double layer" (approximately 400-800 mV vs. RHE) region so that background currents can be neglected in the integration. This could be achieved by either choosing a less positive  $E_{\text{ads}}$  (e.g. 70 mV vs. RHE), or lowering the sweep rate (e.g. 50 mV/sec), or increasing the roughness factor of the electrodes (e.g. platinization) or a combination of the three factors mentioned above.

#### B. Electrochemical Sensing of $\text{CO}_2$ Dissolved in a Liquid Using Platinized Platinum Electrodes

The  $\text{CO}_2$  sensing characteristics were systematically studied as a function of  $t_{\text{ads}}$ , sweep rate, internal electrolyte composition, and external  $\text{CO}_2$  containing solution composition for a wide range of  $P_{\text{CO}_2}$  using the two-electrode sensor with platinized platinum electrodes. In all experiments,  $E_{\text{ads}}$  was fixed at 70 mV (vs. RHE) because it was low enough to favor the efficient formation of "Reduced- $\text{CO}_2$ " species yet high enough to avoid hydrogen evolution. Finally, some of the experiments were repeated using the three-electrode sensor for comparison of the performance of the two sensor configurations.

### 1. Effect of Sweep Rate

The effect of sweep rate on the current-potential response curve in the "Reduced-CO<sub>2</sub>" oxidation region was studied using a two-electrode sensor at three different sweep rates (i.e. 50, 150, and 500 mV/sec) for a wide  $P_{\text{CO}_2}$  range under the same reductive adsorption conditions. (i.e.  $t_{\text{ads}} = 120$  sec,  $E_{\text{ads}} = 70$  mV vs. RHE). 1 M H<sub>2</sub>SO<sub>4</sub> was used both as the internal electrolyte and the external CO<sub>2</sub> containing solution. The results obtained at 500, 150, and 50 mV/sec are shown in Figures 6, 7, and 8, respectively. The peak current was observed in a potential region from 700 to 900 mV vs. RHE with its position shifting towards lower potential at a slower sweep rate. These currents were integrated and the resultant "Reduced-CO<sub>2</sub>" oxidation charges ( $Q_{\text{ox}}$ ) were plotted versus  $P_{\text{CO}_2}$  as shown in Figure 9. It clearly shows that the oxidation charge is practically independent of sweep rate within experimental error. Since it is more desirable for this application to have the "Reduced-CO<sub>2</sub>" current peak in the double layer region due to the negligible background current, the sweep rate of 50 mV/sec was chosen for most of CO<sub>2</sub>-sensing experiments in this program.

### 2. Effect of Adsorption Time

The effect of the reductive adsorption time period ( $t_{\text{ads}}$ ) on the CO<sub>2</sub>-sensing characteristics was also investigated using the two-electrode sensor with 1 M H<sub>2</sub>SO<sub>4</sub> as the internal electrolyte as well as the external CO<sub>2</sub> containing liquid. For  $E_{\text{ads}} = 70$  mV vs. RHE, and sweep rate = 50 mV/sec, we have reduced  $t_{\text{ads}}$  from 120 to 60, 40, and 20 sec. Figure 10 shows the  $Q_{\text{ox}}$  vs.  $P_{\text{CO}_2}$  curves

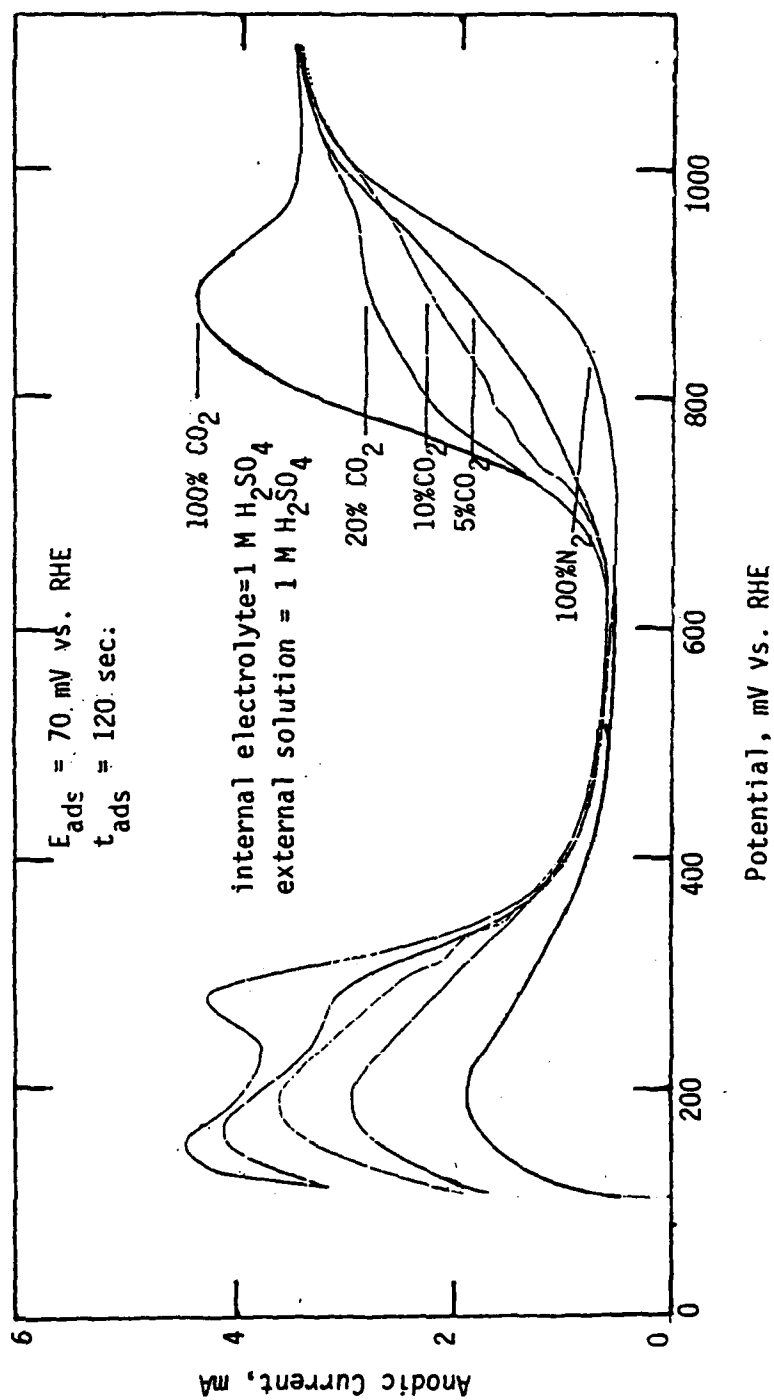


Figure 6. Current-Potential Curves of a Two-Electrode  $\text{CO}_2$  Sensor with Sweep Rate at 500 mV/sec.

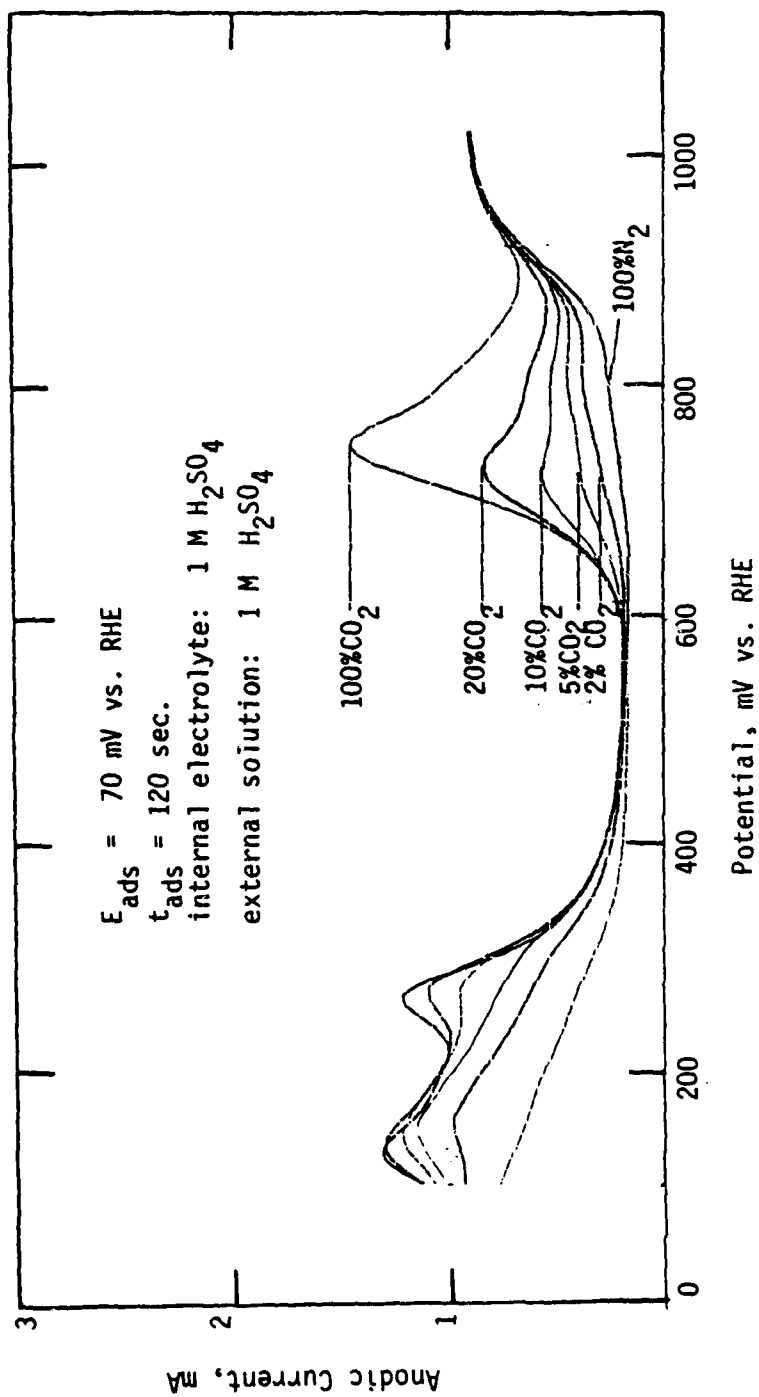


Figure 7. Current-Potential Curves of a Two-Electrode  $\text{CO}_2$  Sensor with Sweep rate at  $150 \text{ mV/sec.}$

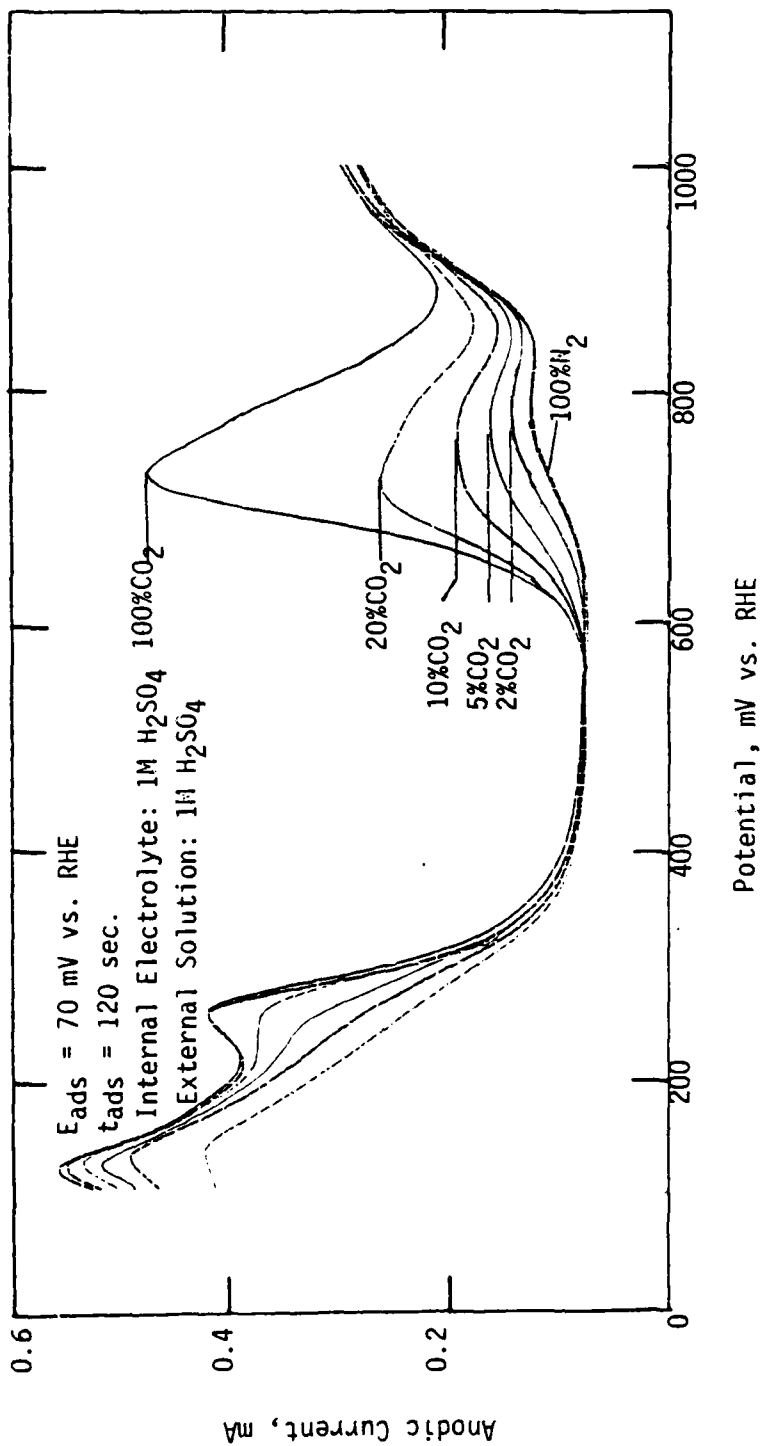


Figure 8. Current-Potential Curves of a Two-Electrode  $\text{CO}_2$  Sensor with Sweep rate at 50 mV/sec.

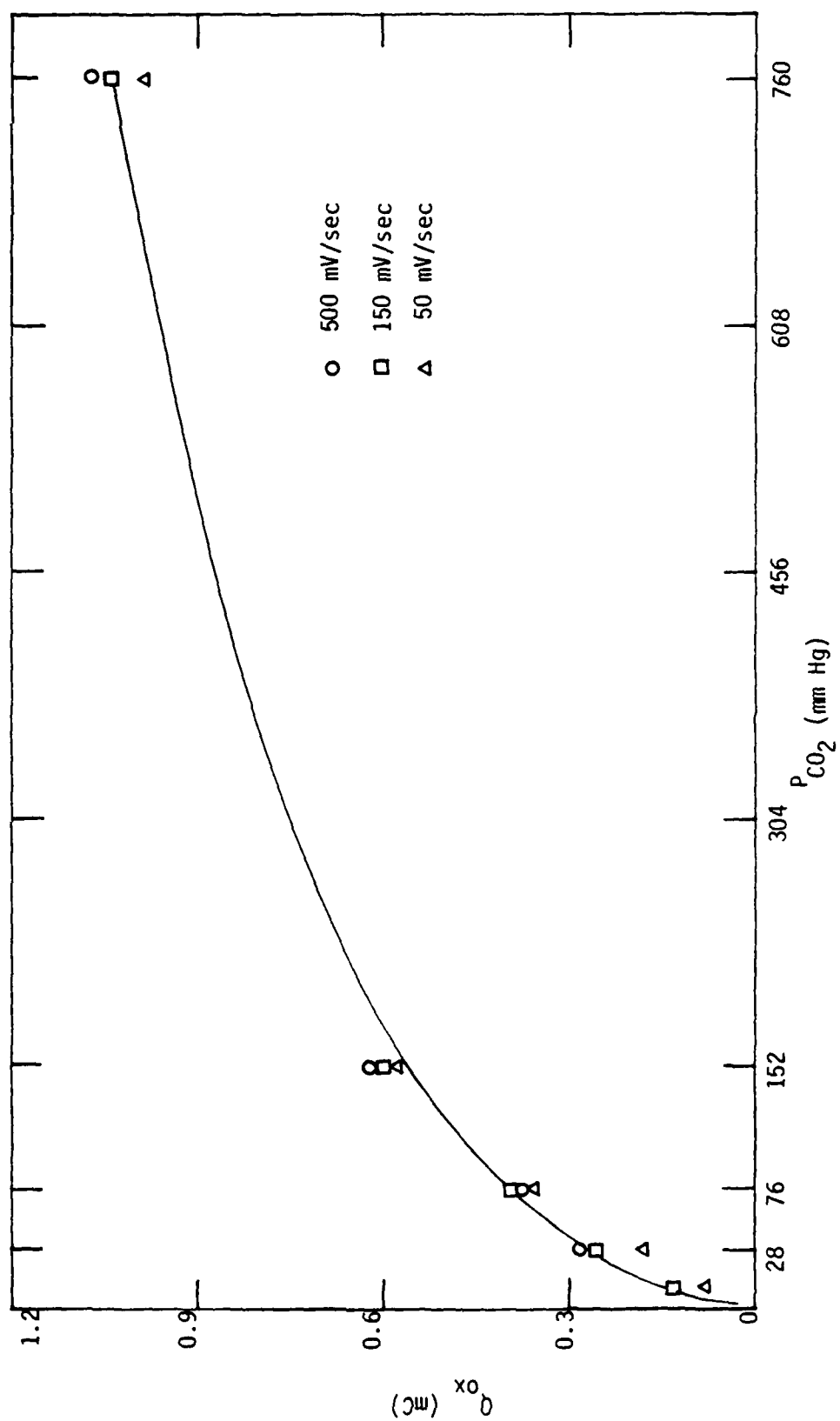


Figure 9.  $Q_{ox}$  vs.  $P_{CO_2}$  at Different Sweep Rates.



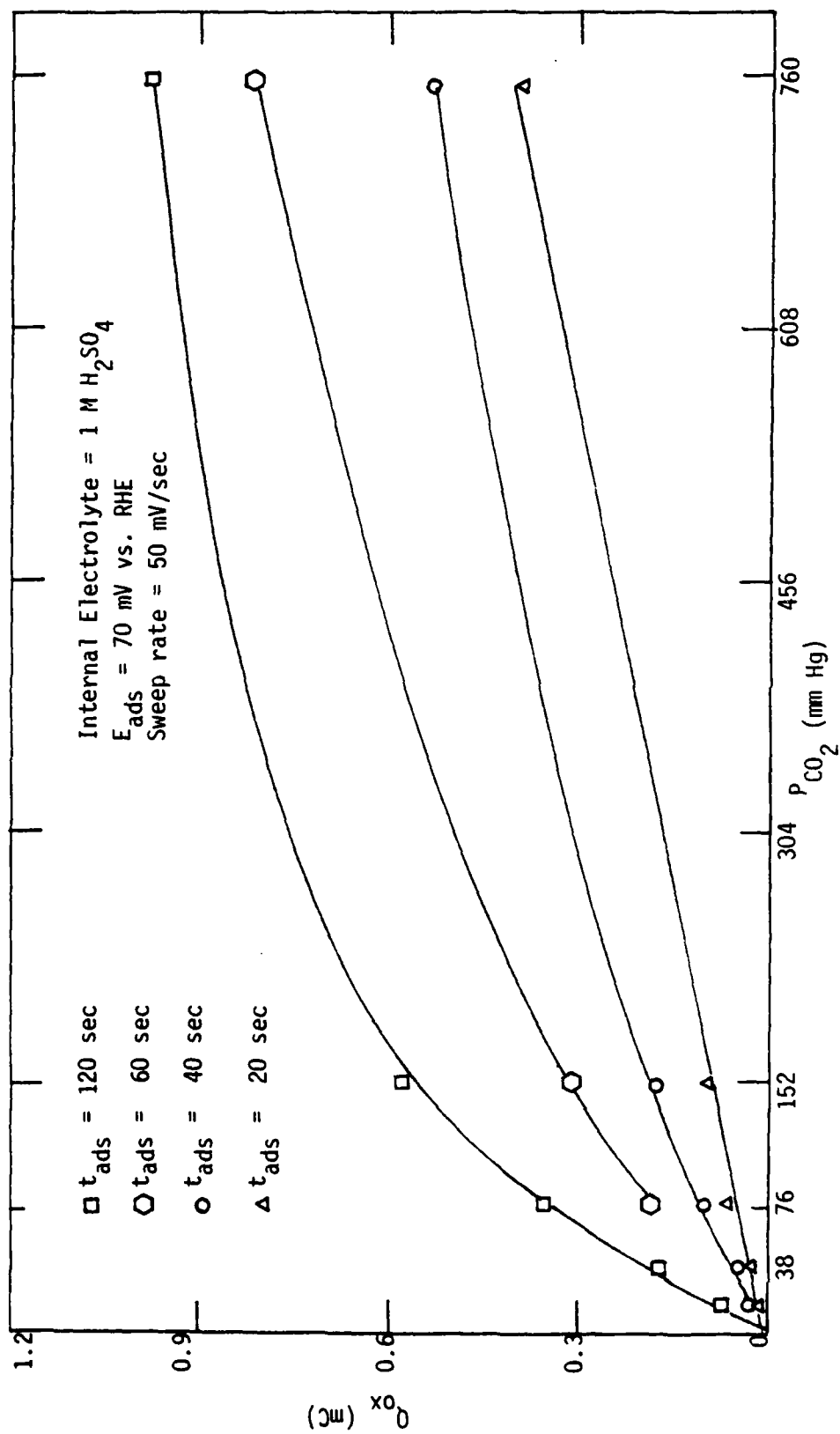


Figure 10.  $Q_{\text{ox}}$  vs.  $P_{\text{CO}_2}$  over 1 M  $\text{H}_2\text{SO}_4$  at 37°C.

obtained at various  $t_{ads}$ . The response was very impressive especially for  $t_{ads} = 20$  sec. In this case, an almost linear relationship was found for a wide  $P_{CO_2}$  range of 8 - 760 mm Hg. Ideally,  $t_{ads}$  should be as short as possible in order to render close to real time reading of  $P_{CO_2}$  and to avoid saturation of electrode surface by "Reduced- $CO_2$ ". In practice,  $t_{ads}$  will have to be carefully chosen so that the sensor response is sensitive enough to accurately quantitatively reflect  $P_{CO_2}$  within the pressure range of interest.

### 3. Effect of Composition of the $CO_2$ Containing Liquid

Similar measurements were made using the two-electrode sensor to determine dissolved  $CO_2$  content in Krebs Ringer Solution. The internal electrolyte was 1 M  $H_2SO_4$ . Figure 11 shows the current-potential curves obtained under the conditions that  $E_{ads} = 70$  mV vs RHE,  $t_{ads} = 40$  sec. and sweep rate = 50 mV/sec for a wide range of  $P_{CO_2}$  from 8 - 760 mm Hg. Clearly, once again the total "Reduced- $CO_2$ " oxidation charge was found to be dependent on the partial pressure of  $CO_2$  in the liquid as shown in Figure 12 (which also shows two other  $Q_{ox}$  vs.  $P_{CO_2}$  curves for  $t_{ads} = 60$  and 120 sec ). Again, we found that the response curve became more linear with shorter  $t_{ads}$ . The sensing capability of dissolved  $CO_2$  remains unaffected by the presence of a different solution across the membrane.

### 4. Effect of Internal Electrolyte Composition

In addition to 1 M  $H_2SO_4$ , three other electrolytes viz.

(a) 0.02 M  $KHCO_3$  and 0.05 M  $Na_2SO_4$ , (b) 0.025 M  $Na_2HPO_4$ , 0.025 M  $KH_2PO_4$ , and 0.1 M  $NaClO_4$ , and (c) 0.05M  $H_2SO_4$  and 0.1 M  $Na_2SO_4$ , were used as

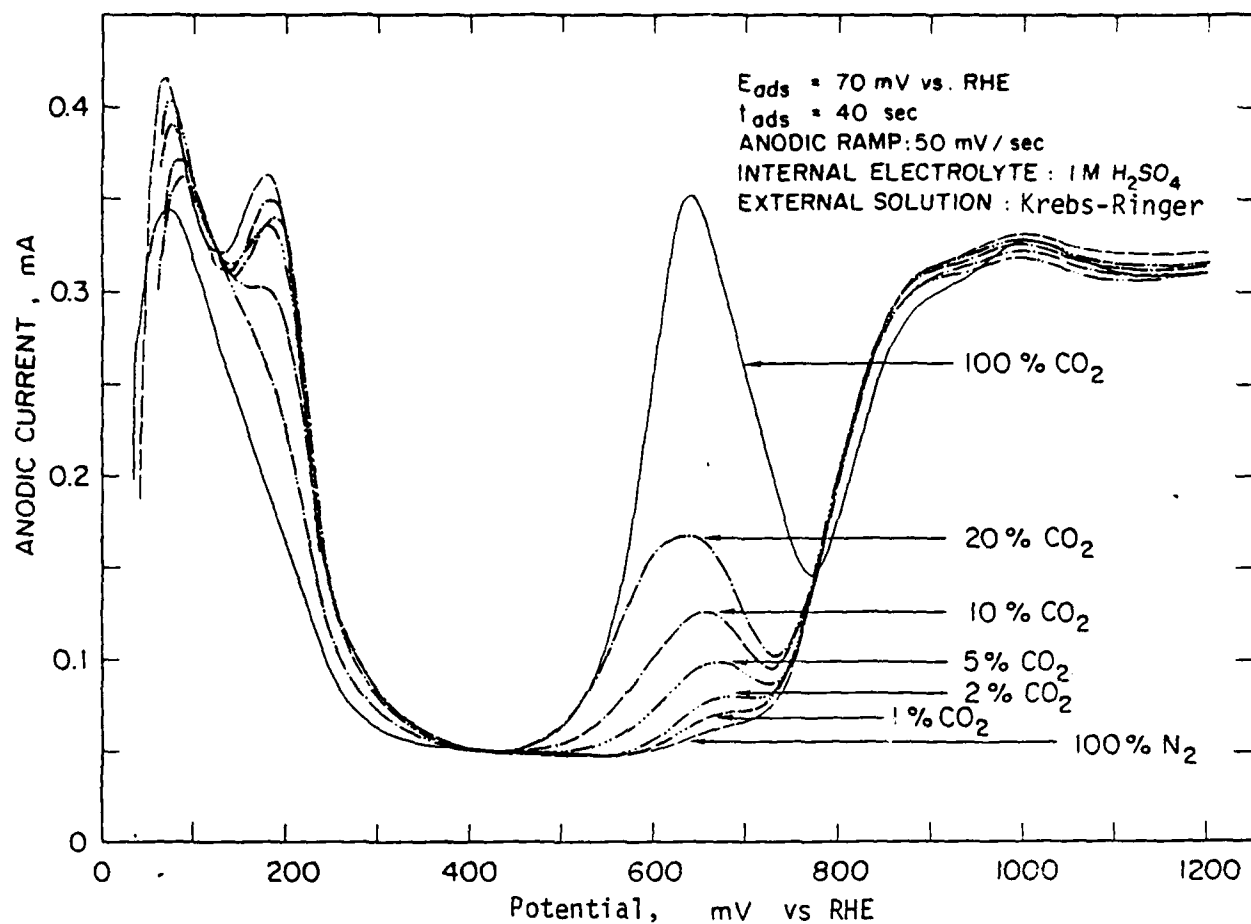


Figure 11 Current-Potential Curves of a Two-Electrode Sensor used to Determine Dissolved  $\text{CO}_2$  in Krebs-Ringer Solution.

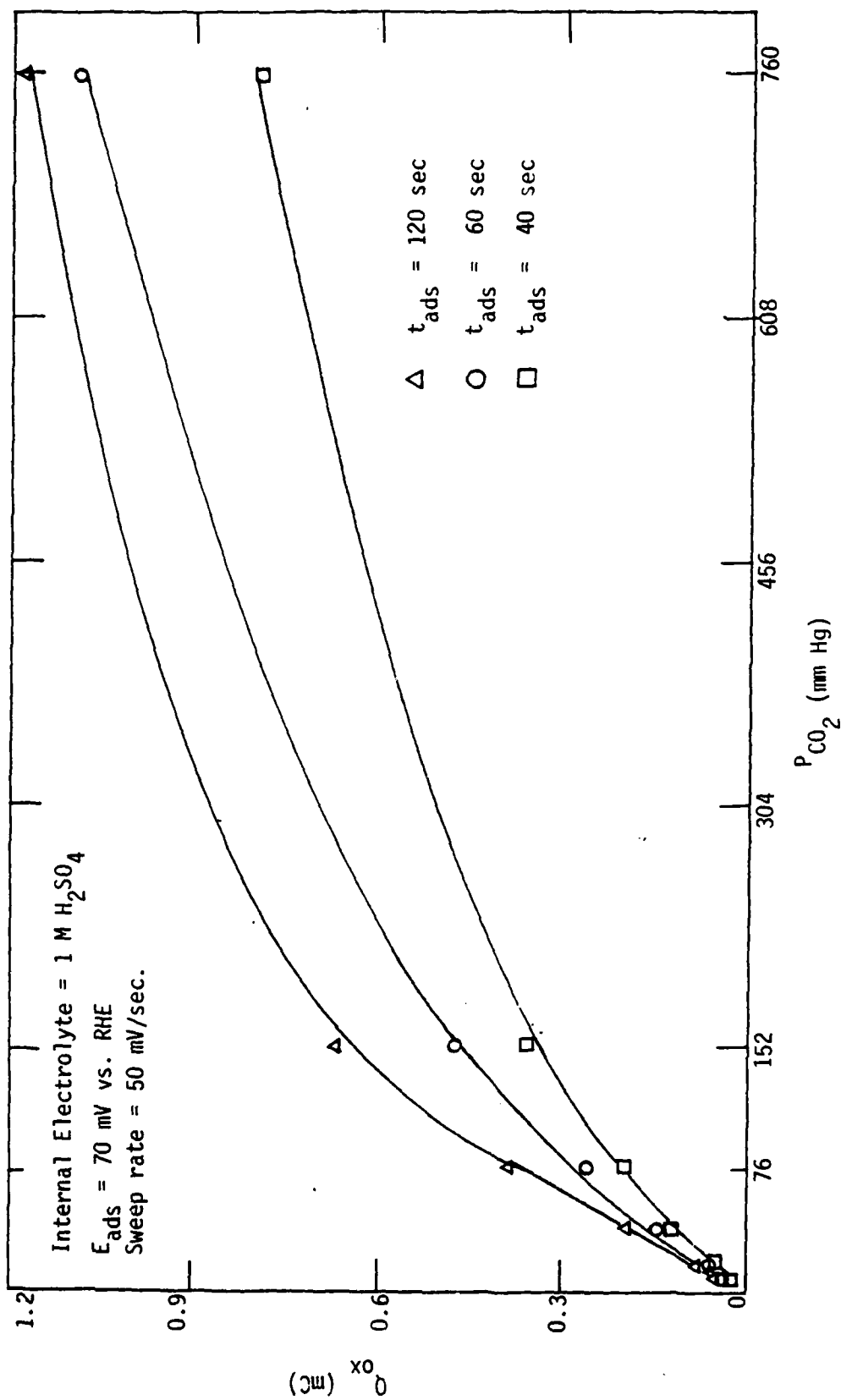
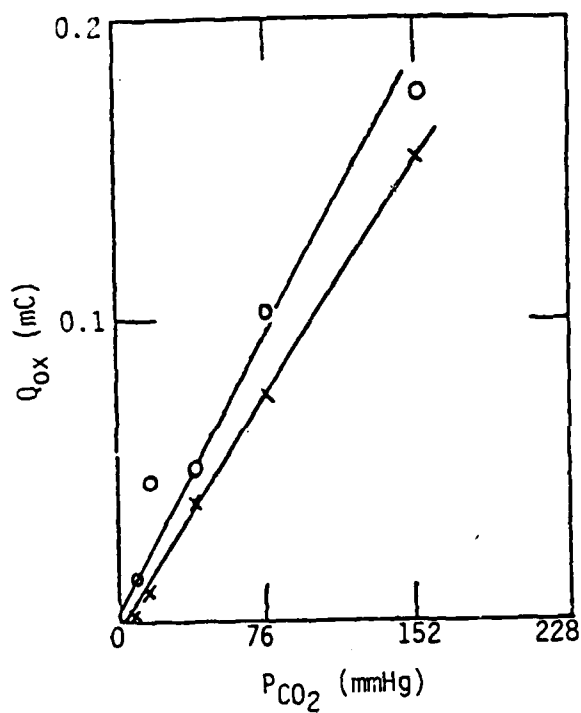


Figure 12.  $Q_{\text{ox}}$  vs  $P_{\text{CO}_2}$  over Krebs Ringer Solution at  $37^\circ\text{C}$ .

internal electrolytes for a two-electrode sensor with platinized platinum electrodes to determine dissolved  $\text{CO}_2$  in Krebs-Ringer solution. For the bicarbonate buffer solution (a) its pH was measured to be 5.9 when saturated with  $\text{CO}_2$  at ambient temperature. The phosphate buffer solution (b) has a measured pH value of 6.5 at  $25^\circ\text{C}$ . Sodium sulfate and sodium perchlorate were added to improve the electrical conductivity of the electrolyte.

The phosphate buffer solution (b) and the dilute sulfuric acid solution (c) gave very similar response curves to the ones obtained in  $1\text{M H}_2\text{SO}_4$ . The "Reduced- $\text{CO}_2$ " oxidation currents were integrated and their corresponding  $Q_{\text{ox}}$  vs.  $P_{\text{CO}_2}$  curves are shown in Figure 13. In both cases, it was possible to operate the sensor at  $t_{\text{ads}} = 5$  sec. to determine  $P_{\text{CO}_2}$  over a wide range of 8-152 mm Hg with accuracy. At a sweep rate of 50 mV/sec, it is thus possible to complete one measurement in less than 15 seconds. Furthermore, we found that the sensitivity of the sensor was not significantly affected by the composition of the internal electrolyte (i.e.  $1\text{M H}_2\text{SO}_4$ , phosphate buffer, and dilute sulfuric acid).

The bicarbonate buffer solution (a), however, behaved quite differently. Typically, two anodic oxidation current peaks, one at  $-300\text{mV}$ , and the other at  $+300\text{mV}$  (vs.SCE), were observed. The reason for this behavior is not yet clear, but in any event, this type of response is not desirable for  $\text{CO}_2$  sensing applications because it tends to complicate the data analysis process.



$E_{ads} = 70 \text{ mV vs. RHE}$

$t_{ads} = 5 \text{ sec.}$

Sweep Rate = 50 mV/sec.

Internal Electrolyte:

(x) phosphate buffer solution (c)

(o) dilute sulfuric acid (d)

External Solution: Krebs Ringer

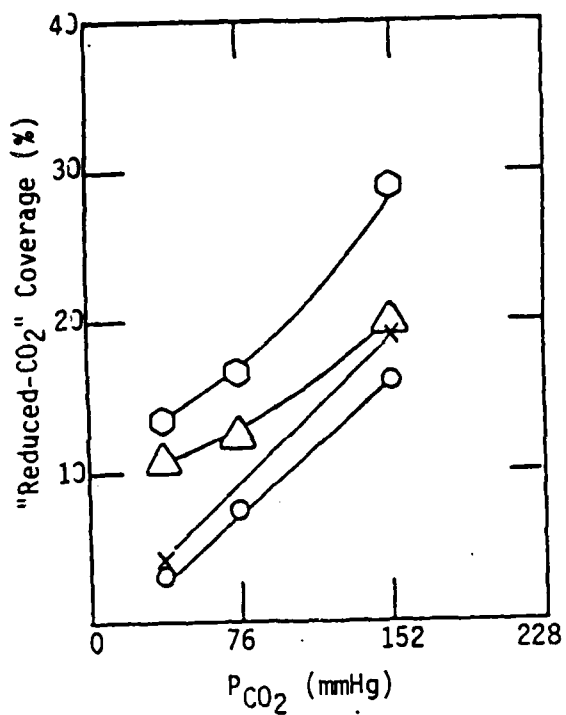
Figure 13.  $Q_{ox}$  vs.  $P_{CO_2}$  Curves Obtained Using Other Internal Electrolytes.

### 5. Effect of Sensor Configuration

The three-electrode "self-contained sensor was also used to measure dissolved  $\text{CO}_2$  in 1 M  $\text{H}_2\text{SO}_4$ , and the response curves obtained were very similar to the ones shown in Figure 8. The results are presented in terms of "Reduced- $\text{CO}_2$ " coverage which is obtained by dividing the measured "Reduced- $\text{CO}_2$ " oxidation charge per unit real electrode surface area by  $220 \mu\text{C}/\text{cm}^2$  (8). A comparison of sensor behavior under the same experimental conditions is shown in Figure 14 which indicates that the parallel rectangular electrode configuration for the two-electrode sensor design was more efficient in terms of "Reduced- $\text{CO}_2$ " formation (than the three-electrode sensor design) most probably due to the more favorable current distribution pattern. It is, however, possible to fabricate a three-electrode self-contained sensor using the same parallel rectangular electrode design if necessary. With regard to the effect of the spacer, as expected, the sensitivity of the sensor was found to be consistently higher without the spacer.

### 6. Effect of Membrane

In most of our experiments, a 25 micron thick Teflon membrane (Gortex, W.L. Gore & Assoc. Inc.) with 0.2 micron pore size was used to separate the internal electrolyte from external environment to protect the sensing electrode from contamination. This membrane was found to perform extremely well. A similar type of membrane with 0.45 micron pore size was also satisfactory. Teflon membranes with pore size larger than 1.0 micron could not be used because they become electrolyte permeable to a certain



$E_{ads} = 70 \text{ mV vs. RHE}$   
 $t_{ads} = 60 \text{ sec.}$

- Two Electrode Sensor without spacer
- △ Two Electrode Sensor with Spacer
- × Three Electrode Sensor without Spacer
- Three Electrode Sensor with Spacer

Figure 14. Comparison of Sensor Configurations; "Reduced-CO<sub>2</sub>" Coverage vs. PCO<sub>2</sub>



extent. The use of a commercial FEP membrane specifically designed for a Clark oxygen sensor was also explored. We were unable to obtain any "Reduced-CO<sub>2</sub>" oxidation response using a sensor covered by such a membrane. The CO<sub>2</sub> permeability of this material must be very low and it is then not suitable for CO<sub>2</sub> sensor applications.

C. Electrochemical Sensing of Carbon Dioxide in a Gas Stream

The capability of a three-electrode sensor to detect CO<sub>2</sub> in gas phase was also demonstrated experimentally. The current-potential response curves obtained during the measuring potential pulse were found to be very similar to the ones reported earlier in the case of measuring CO<sub>2</sub> dissolved in a liquid. The "Reduced-CO<sub>2</sub>" oxidation charge in a CO<sub>2</sub>/N<sub>2</sub> mixture was plotted against  $P_{CO_2}$  and shown in Figure 15.

D. Electrochemical Sensing of CO<sub>2</sub> and O<sub>2</sub> Using the Same Sensor

The capability of this electrochemical method to concurrently but independently measure CO<sub>2</sub> and O<sub>2</sub> was also demonstrated experimentally. The same reductive adsorption ("Reduced-CO<sub>2</sub>" formation) and anodic potential sweep ("Reduced-CO<sub>2</sub>" oxidation) steps were used to measure  $P_{CO_2}$ . After reaching the most positive potential of the triangular sweep (i.e. at the beginning of the cathodic sweep), oxygen reduction limiting currents were measured at ~500 mV vs. RHE. These limiting currents were plotted against  $P_{CO_2}$  and a linear relationship was found (see Figure 16). Since the measuring of  $P_{CO_2}$  is done using

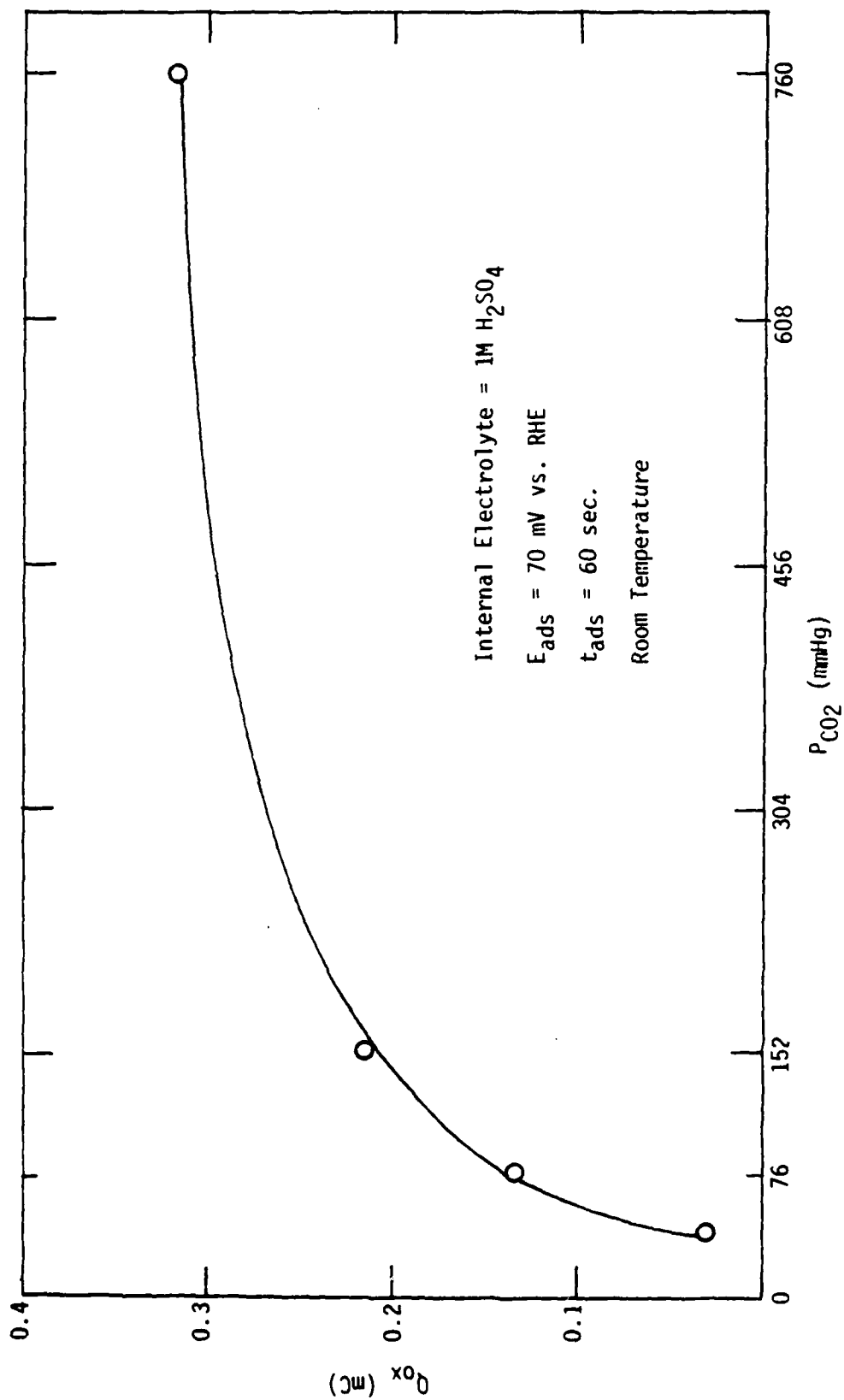


Figure 15. Q<sub>ox</sub> vs. P<sub>CO2</sub> in Gas Phase.

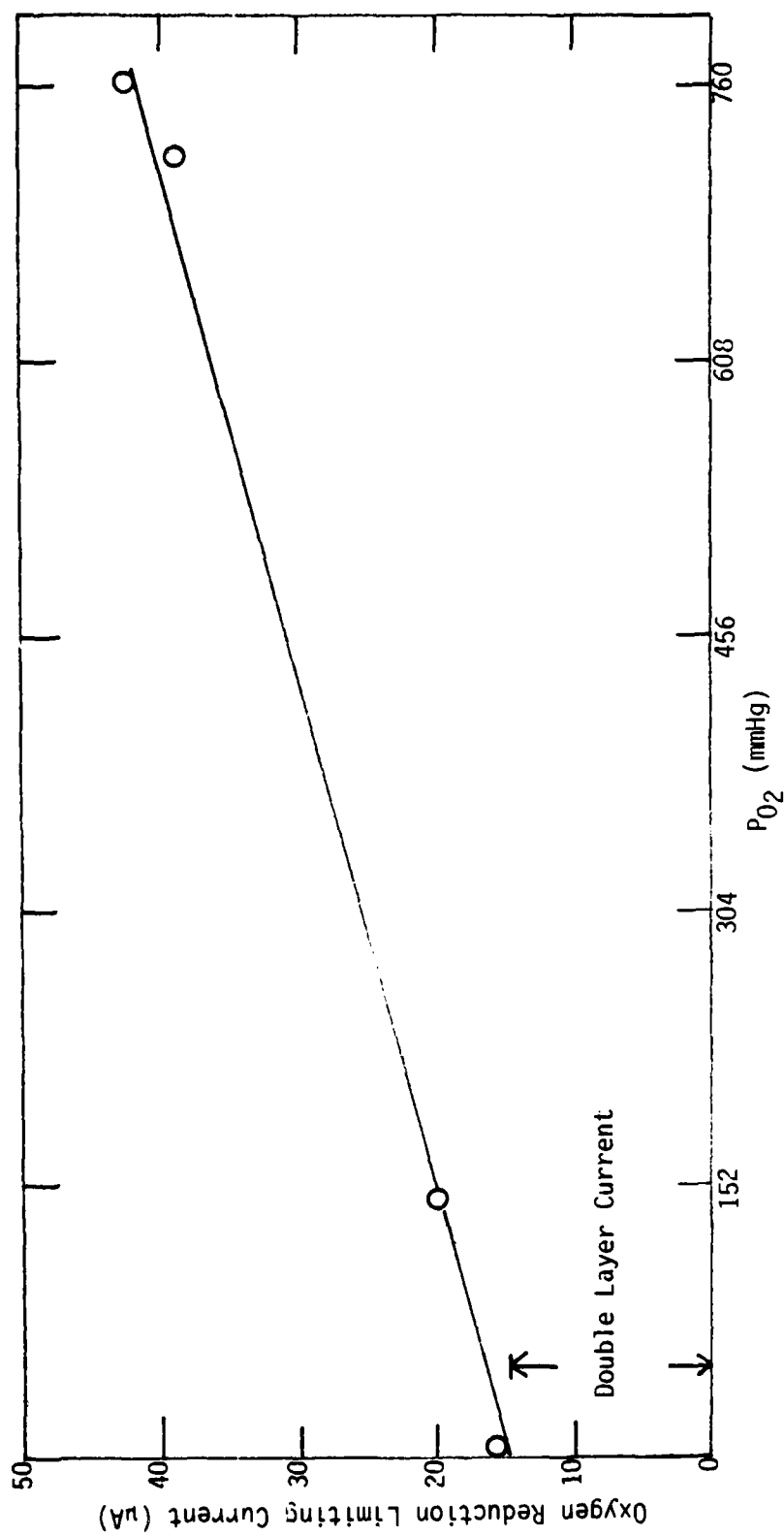


Figure 16. Oxygen Reduction Limiting Current vs.  $P_{O_2}$ .

a charge method, under conditions such that the oxygen reduction current can be excluded, and the oxygen reduction limiting current is measured at a high potential at which "Reduced-CO<sub>2</sub>" does not form, the interference between CO<sub>2</sub> and O<sub>2</sub> was found to be minimal.

#### IV. CONCLUSIONS AND WORK PLAN FOR PHASE II

The feasibility of developing a new electrochemical carbon dioxide sensing method based on the reductive adsorption of  $\text{CO}_2$  on platinum and the subsequent anodic oxidation of "Reduced  $\text{CO}_2$ " species has been successfully proven in this program. Laboratory prototype sensors were designed and fabricated using a two-electrode sensor configuration suitable for measuring  $\text{CO}_2$  dissolved in a liquid in conjunction with an external reference electrode and a three-electrode "self-contained" sensor configuration capable of sensing  $\text{CO}_2$  in liquids as well as in gases. Since these sensors are basically modified Clark oxygen electrodes with sophisticated control electronics, they are certainly conducive to miniturization and implantation.

The substantially concurrent but independent measurement of  $\text{CO}_2$  and  $\text{O}_2$  was also demonstrated experimentally using a laboratory prototype sensor. This additional option enables the detection of  $\text{CO}_2$  and  $\text{O}_2$  using the same sensor which is especially attractive for biomedical application.

In the second phase of the program, we plan to continue optimizing the sensor construction and electrical parameters to obtain rapid, reliable, and reproducible measurements of  $P_{\text{CO}_2}$  in either liquids or in gases. We intend to devote our efforts to the packaging of this newly developed sensor for durability and reliability. This, of course, will include miniaturization of the sensor. As for the electronic control instrument, a laboratory prototype  $P_{\text{CO}_2}$  meter consisting of a potentiostat, a function generator, and an integrator has been designed and

constructed by Giner, Inc. at no direct cost to the Phase I program. We propose to further develop this electronic instrument to the extent that a prototype device suitable for field test can be designed and built. Eventually, a  $P_{CO_2}$  meter unit suitable for commercialization will be designed. Other areas yet to be studied in detail include the interaction with other coreactants, reliability of the sensor, reproducibility from sensor to sensor, the actual response time of the sensor, and the lifetime of the sensor. On the basis of results obtained to date, it is envisioned that this new electrochemical  $CO_2$  sensor can be completely developed, at least for certain specific applications, within the Phase II program.

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